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CRYSTAL STRUCTURE OF COPPER FLUOSILICATE HEXAHYDRATE

Siddhartha Ray, Allan Zalkin, and David H. Templeton

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Crystal Structure of Copper Fluosilicate Hexahydrate*

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Contrary to earlier belief, copper fluosilicate hexahydrate (space group $R\bar{3}$) is not isomorphous with $NiSnCl_6 \cdot 6H_2O$, having a four times larger primitive cell with $\underline{a}$ = 10.998 ± .002 Å, α = 111°29' ± 3', Z = 4. For the hexagonal cell, $\underline{a}$ = 18.180(2) and $\underline{c}$ = 9.857(2) Å. Using 592 independent X-ray data collected by a counter method, the structure has been refined to a conventional R = .04. The structure consists of two types of columns, both made up by alternate stacking of $Cu(H_2O)_6$ and SiF_6 octahedra along the direction of the 3-fold axis, but while the SiF_6 octahedra are regular in both types of columns, $Cu(H_2O)_6$ octahedra are regular in one with Cu-O = 2.074(7) Å (one-fourth of the copper atoms) and tetragonally distorted in the other with Cu-O = 1.970(7) Å (four neighbors) and 2.367(7) Å (two neighbors) (three-fourths of the copper atoms).

*Work performed under the auspices of the U.S. Atomic Energy Commission.

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In a previous communication (Ray, Zalkin & Templeton, 19xx) we mentioned the diverse structures which exist for the fluosilicate hexahydrates of divalent metals, which earlier had been believed to be like the structure determined by Pauling (1930) for $NiSnCl_6 \cdot 6H_2O$. In the present paper we describe the structure of $CuSiF_6 \cdot 6H_2O$, which is significantly different from all the others.

Experimental

Copper fluosilicate was prepared by dissolving metallic copper in fluosilicic acid. On slow evaporation at room temperature (~23°C), deep blue crystals of the hexahydrate appeared, which were recrystallized from aqueous solution. The crystals obtained were susceptible to rapid efflorescence on exposure to the atmosphere (relative humidity ~50%).

The specimen selected was of a prismatic habit, with both height and thickness ~0.2 mm. It was quickly sealed off in a quartz capillary, and a Laue photograph showed that it was unaffected by the brief exposure to air. The crystal, mounted nearly along the c-axis, was transferred to a Picker FACS-I four-circle automatic diffractometer. A graphite monochromator was used, and a scintillation counter equipped with pulse-height

discriminator served as the detector. Eleven Cu $\underline{K}\alpha_1$ (λ = 1.54051 Å) reflections were successively centered on the aperture of the detector, and the corresponding angular settings were used for a least-squares refinement of the cell dimensions.

Intensity data were collected using Mo $\underline{K}\alpha$ radiation, and a θ-2θ scan. The scan was started 0.8° below the $\underline{K}\alpha_1$ peak, and continued to 0.8° beyond the $\underline{K}\alpha_2$ peak for each reflection. Background was counted for 10 sec at each end of the scan. Two standard reflections were checked at regular intervals. During the first attempt of data collection, the intensity of the standards diminished systematically due to slow change in the orientation of the crystal. During the collection of another data set, which was finally accepted as satisfactory, standards were checked every hour. Whenever perceptible change in the orientation of the crystal was apparent the orientation matrix was recalculated. This occurred at intervals of about six hours.

All of the reflections with positive ℓ and $0° < 2\theta \leq 40°$ were thus scanned. A total of 1868 data were collected, of which 592 were independent; 235 of these had intensity less than the standard deviation, and were given zero weight in the least-squares refinement.

Structure factors and their standard deviations were derived as described by Fischer, Zalkin & Templeton (1970) with p = 0.05. No correction was made for absorption (μ = 26.1 cm^{-1} for Mo $K\alpha$ radiation). We used the spherical hydrogen form factors of Stewart, Davidson & Simpson (1965) and form factors of other neutral atoms of Cromer & Waber (1965) with dispersion corrections of Cromer (1965).

Crystal Data

$CuSiF_6 \cdot 6H_2O$: deep blue prisms.

Hexagonal cell constants: a = 18.180 ± .002 Å, c = 9.857 ± .002 Å.

Rhombohedral cell constants calculated from the above:

a = 10.998 ± .002 Å, α = 111°29' ± 3'.

Four formula units per rhomobhedral cell.

Space group: $R\bar{3}$.

D_m = 2.207 g cm^{-3}, D_x = 2.215 g cm^{-3}.

Determination of the Structure

It was assumed that, as in other hexahydrated fluosilicates, this structure consists of columns, extending in the c direction, built up of alternating $Cu(H_2O)_6$ and SiF_6 octahedra. But in this case the neighboring columns are not identical, and the cell dimensions are doubled in the plane normal to the 3-fold axis. Accordingly the

Cu and Si atoms were given the following special positions in the hexagonal cell:

$$(0,0,0;\ 1/3,2/3,2/3;\ 2/3,1/3,1/3) +$$

Cu(1) at 0,0,0;

Cu(2) at 1/2,0,0; 0,1/2,0; 1/2,1/2,0;

Si(1) at 0,0,1/2;

Si(2) at 1/2,0,1/2; 0,1/2,1/2; 1/2,1/2,1/2.

Four independent atoms each of O and F were assigned general positions. Cu(1) with site symmetry $\bar{3}$, was surrounded by six equivalent O(1); each of the Cu(2), with site symmetry $\bar{1}$, was surrounded by O(2), O(3), O(4) and their centrosymmetric equivalents related by inversion through the position of the particular Cu(2). Similar labelling was adopted for Si and F.

A Patterson map indicated that while the oxygen octahedra surrounding Cu(1) and Cu(2) had the same orientation, there were two possible orientations for the corresponding SiF_6 octahedra. After some initial set-back in the matter of choice, all the O and F atoms were assigned satisfactory positions, so that least-squares refinement with isotropic temperature factors ended up with an $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ value of .078. With anisotropic temperature factors for all the atoms, R dropped to .055.

A difference map was computed, and attempts were made to locate the hydrogen atoms. Although the map showed positive peaks at the expected positions of hydrogen atoms, the largest positive peaks seemed to be due to inadequate description of thermal motion. Attempt to refine the positions and thermal parameters of hydrogen atoms was unsuccessful. However, when the hydrogen atoms were held fixed in their calculated positions, varying only their common isotropic thermal parameter, further refinement reduced $\underline{R}$ to 0.040 (0.077 including zero-weighted data), $\underline{R}_2 = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$ to 0.043, and the goodness of fit to 1.12. In the last cycle, no parameter shifted more than 0.005σ.

The final coordinates and thermal parameters are given in Tables 1 and 2. The observed and calculated structure factors are listed in Table 3. Some interatomic distances and bond angles appear in Tables 4 and 5.

Discussion

It is interesting to compare the present structure with that of $CoSiF_6 \cdot 6H_2O$, as described in our previous communication (Ray et al., 19xx). The basic features in both the cases are the columns of alternating octahedra. In the cobalt compound we have two disordered positions unequally occupied by the fluorine atoms. In the present

case, there is no disorder; instead, we have two very different types of column appearing alternately along the hexagonal a-axis. The columns of the first type, containing Cu(1) and Si(1) atoms, have the $\bar{3}$ axes passing through them. The constituent $Cu(H_2O)_6$ and SiF_6 octahedra are regular within the experimental limits, and oriented in the same way as the corresponding octahedra in $CoSiF_6 \cdot 6H_2O$, with the fluorine in the position with lower occupancy. The neighboring column, containing Cu(2) and Si(2), both with site symmetry $\bar{1}$, is very different. While the SiF_6 octahedron is still almost regular, there is a distinct tetragonal distortion in the $Cu(H_2O)_6$ octahedron. This is very significant, because previously $CuSiF_6 \cdot 6H_2O$, like the other hexahydrated fluosilicates, was supposed to be isomorphous with $NiSnCl_6 \cdot 6H_2O$, with one formula unit per rhombohedral unit cell, and consequently, the water octahedron surrounding the Cu^{++} ion was considered trigonally distorted. With such assumption, Bleany & Ingram (1950) used mixed crystals of $CuSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6H_2O$ in their study of paramagnetic resonance, and Abragam & Pryce (1950) gave theoretical interpretation of the results thus obtained, assuming that the Cu^{++} ion was subjected to a ligand field of trigonal symmetry. The Cu:Zn ratio in the mixed crystal used in the experiment has not been mentioned in the paper of Bleaney & Ingram.

Assuming that the Cu^{++} ion concentration was very low, it is quite probable that the structure of the mixed crystal resembled that of $ZnSiF_6 \cdot 6H_2O$, and consequently the Cu^{++} ions may indeed have been in a ligand field with trigonal symmetry. In that case, there should be no objection to the said studies, except that the results obtained do not relate to the actual ligand field in $CuSiF_6 \cdot 6H_2O$. A careful study of paramagnetic resonance with the "undiluted" salt would then be worthwhile. It would also be interesting to prepare mixed crystals with different Cu:Zn ratio, and find out for what maximum concentration of Cu^{++} the structure resembles that of $ZnSiF_6 \cdot 6H_2O$.

Figure 1 shows a portion of the structure in orthogonal projection on the xz-plane. One of each kind of hydrogen atom is identified. The bonds O(1)···F(1) and O(1)···F(2) follow the same pattern as in $CoSiF_6 \cdot 6H_2O$. But while each of F(1), F(2) and F(3) takes part in two hydrogen bonds, F(4) seems to participate in only one; there appears an O(3)···O(4) bond instead. This makes the hydrogen bond configuration in this case rather different than that in $CoSiF_6 \cdot 6H_2O$, where each F atom participates in two hydrogen bonds.

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Table 1. Coordinates

Estimated standard deviations of the least significant digits are in parentheses. Hydrogen coordinates were not refined.

	x	y	z
Cu(1)	0	0	0
Cu(2)	.5000	0	0
Si(1)	0	0	.5000
Si(2)	.5000	0	.5000
F(1)	.0795(4)	.0703(4)	.4015(5)
F(2)	.4099(4)	.2068(5)	.2844(6)
F(3)	.2676(4)	.1747(4)	.2743(7)
F(4)	.3032(5)	.0699(4)	.2253(7)
O(1)	.0976(4)	.0887(4)	.1207(7)
O(2)	.2522(4)	.4268(4)	.4453(7)
O(3)	.0769(5)	.3357(4)	.4418(7)
O(4)	.1749(5)	.2381(4)	.4881(7)
H(1)	.0920	.0820	.2110
H(2)	.1500	.1000	.0960
H(3)	.2350	.4210	.5330
H(4)	.3010	.4280	.4430
H(5)	.0740	.3820	.4260
H(6)	.0330	.2840	.4640
H(7)	.1500	.2470	.5600
H(8)	.1440	.1840	.4600

Table 2. Anisotropic thermal parameters, $Å^2$

The form of the temperature factor is $\exp[-(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \cdots)/4]$. The common isotropic thermal parameter for hydrogen refined to $B = 3.9 \pm 1.0$ $Å^2$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	1.9(1)	1.9	1.3(2)	.95	0	0
Cu(2)	2.1(1)	2.2(1)	1.81(9)	1.14(9)	.00(8)	-.33(8)
Si(1)	2.4(3)	2.4	.8(3)	1.2	0	0
Si(2)	1.6(2)	1.9(2)	1.9(2)	.9(2)	-.3(2)	-.1(2)
F(1)	2.3(3)	3.4(3)	2.1(3)	1.1(2)	.7(2)	.5(2)
F(2)	2.4(3)	7.7(4)	2.2(3)	2.2(3)	-.8(2)	-1.2(3)
F(3)	3.3(3)	6.8(4)	3.3(3)	3.4(3)	.0(3)	-1.0(3)
F(4)	6.5(5)	3.1(4)	6.7(5)	1.7(3)	-.3(4)	1.5(3)
O(1)	2.6(4)	3.8(4)	1.6(3)	1.2(3)	-.1(3)	-.0(3)
O(2)	2.9(4)	2.6(4)	2.3(4)	1.1(3)	-.4(3)	-.9(3)
O(3)	3.5(4)	1.7(4)	4.3(5)	1.5(3)	.8(3)	-.1(3)
O(4)	4.5(5)	2.9(4)	2.3(4)	2.3(4)	.2(3)	-.4(3)

Table 3. Observed and calculated structure factors

Reflections marked with an asterisk had $I < \sigma(I)$ and were given zero weight.

(Table to be reproduced photographically.)

Table 3. Observed and calculated structure factors. Data where $I < \sigma(I)$ are marked with asterisk.

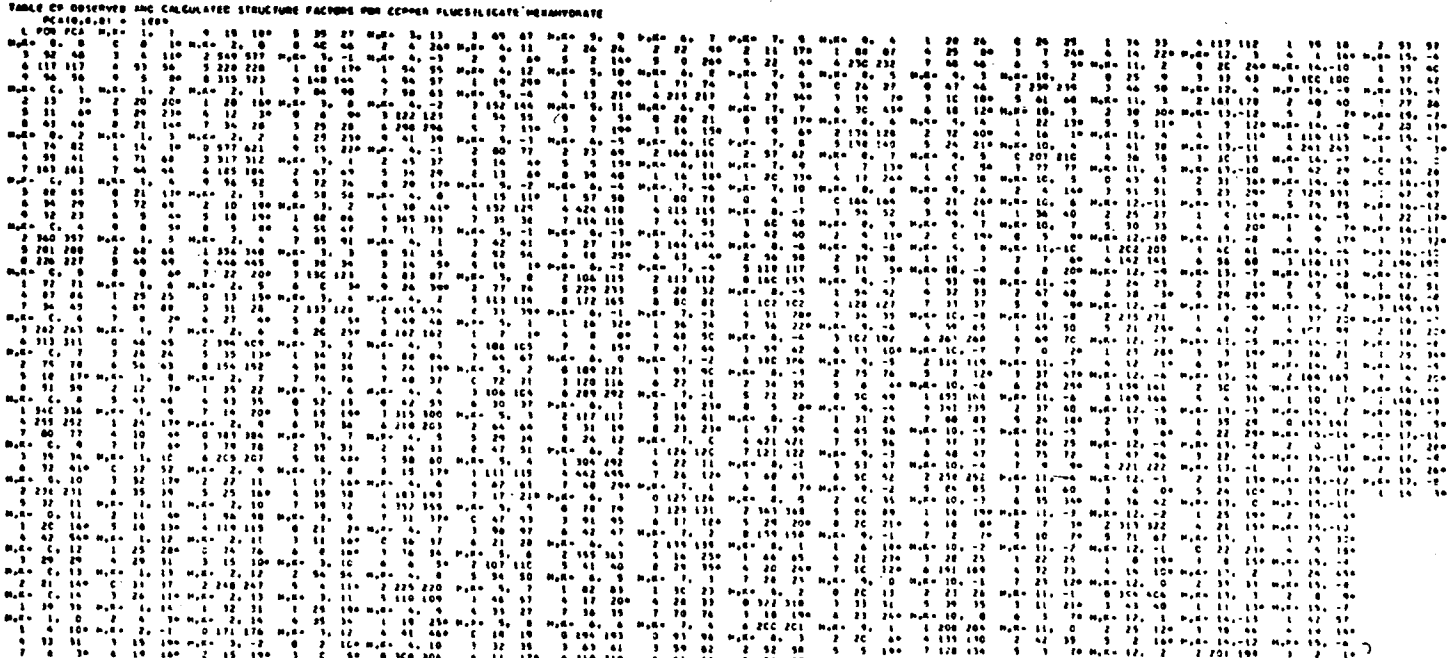

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Table 4. Interatomic distances, Å

Uncorrected distances are given, some followed within parentheses by values corrected for thermal motion assuming that the lighter atom rides on the heavier atom.

A. Distances in octahedra.

Cu(1)-O(1)	2.074 ± .007 (2.083)
Cu(2)-O(2)	1.970 ± .007 (1.978)
Cu(2)-O(3)	1.970 ± .007 (1.978)
Cu(2)-O(4)	2.367 ± .007 (2.374)
Si(1)-F(1)	1.679 ± .005 (1.690)
Si(2)-F(2)	1.674 ± .006 (1.704)
Si(2)-F(3)	1.659 ± .006 (1.684)
Si(2)-F(4)	1.663 ± .006 (1.705)

B. Distances involved in hydrogen bonds (arranged according to the serial number of the hydrogen atom involved).

O(1)-F(1)	2.79 ± .01
O(1)-F(2)	2.71 ± .01
O(2)-F(2)	2.78 ± .01
O(2)-F(4)	2.69 ± .01
O(3)-F(3)	2.99 ± .01
O(3)-O(4)	2.84 ± .01
O(4)-F(3)	2.97 ± .01
O(4)-F(1)	2.78 ± .01

Table 5. Bond angles, deg

O(1)-Cu(1)-O(1)	90.4 ± 0.4
O(1)-Cu(1)-O(1)	89.6 ± 0.4
O(2)-Cu(2)-O(3)	89.0 ± 0.4
O(2)-Cu(2)-O(4)	87.7 ± 0.3
O(3)-Cu(2)-O(4)	91.3 ± 0.3
F(1)-Si(1)-F(1)	89.9 ± 0.3
F(1)-Si(1)-F(1)	90.1 ± 0.3
F(2)-Si(2)-F(3)	89.8 ± 0.4
F(2)-Si(2)-F(4)	89.0 ± 0.4
F(3)-Si(2)-F(4)	90.0 ± 0.4
F(1)---O(1)---F(2)	109.6 ± 0.3
F(2)---O(2)---F(4)	106.4 ± 0.3
F(3)---O(3)---O(4)	124.5 ± 0.3
F(3)---O(4)---F(1)	110.2 ± 0.3

Figure Caption

Fig. 1. Structure of $CuSiF_6 \cdot 6H_2O$, orthogonal projection on xz-plane.

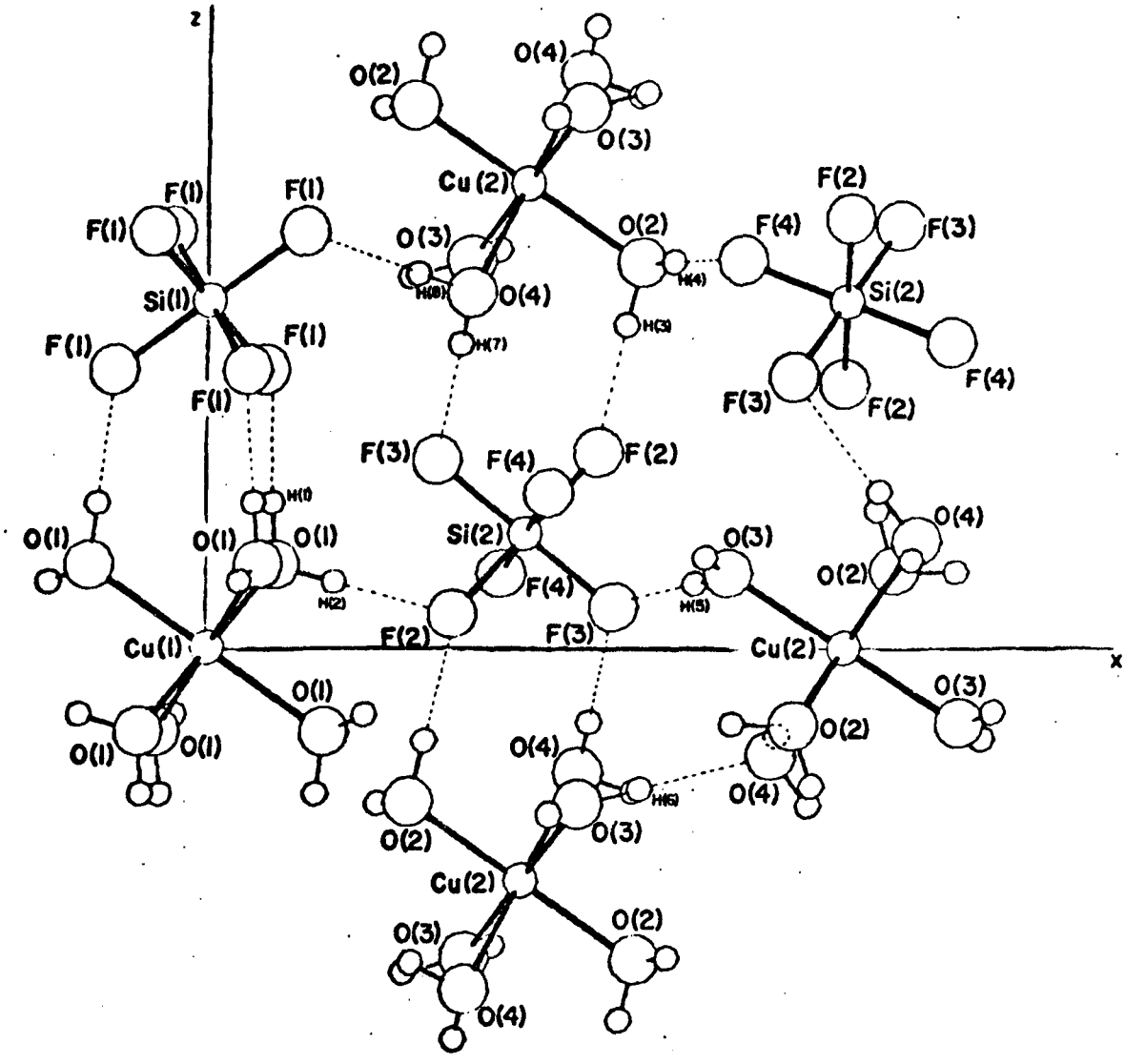

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Fig. 1.

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